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¹⁷O NMR Study of the Intrinsic Magnetic Susceptibility and Spin Dynamics of the Quantum Kagome Antiferromagnet ZnCu₃(OH)₆Cl₂

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We report, through ¹⁷O NMR, an unambiguous local determination of the intrinsic kagome lattice spin susceptibility as well as that created around nonmagnetic defects arising from natural Zn/Cu exchange in the $S = 1/2$ (Cu²⁺) herbertsmithite ZnCu₃(OH)₆Cl₂ compound. The issue of a singlet–triplet gap is addressed. The magnetic response around a defect is found to markedly differ from that observed in nonfrustrated antiferromagnets. Finally, we discuss our relaxation measurements in the light of Cu and Cl NMR data and suggest a flat q dependence of the excitations.

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When nearest neighbor interacting $1/2$ spins decorate the vertices of corner-sharing triangles, as in the kagome antiferromagnet (AFM), the geometry of the lattice frustrates the magnetic interactions and the classical Néel states are destabilized. Since Anderson's seminal idea of a resonating valence bond spin liquid state [1], the nature of the actual ground state has been the subject of extensive theoretical work over the past 15 years [2–10] with no definitive conclusion so far. In contrast, there has been relatively little experimental work on quantum kagome antiferromagnets, and what has been carried out has not provided clear insight into the nature of the ground state [11]. The main reason for this lag is that achieving well decoupled perfect kagome planes has represented a real challenge since the pioneering work on kagome bilayers in SrCr₈Ga₄O₁₉ [12].

Quite recently the end member ($x = 1$) of the paratacamite family Zn _{x} Cu_{4– x} (OH)₆Cl₂, known as herbertsmithite, after the mineral with this composition and structure, was revealed as a “structurally perfect $S = 1/2$ kagome antiferromagnet” [13] and provided a new experimental opportunity to test theory. Because of a more favorable electrostatic environment, Cu²⁺ is expected to preferentially occupy the distorted octahedral kagome sites. Therefore ZnCu₃(OH)₆Cl₂ could feature perfect Cu²⁺, $S = 1/2$, kagome planes separated by nonmagnetic Zn²⁺ layers (Fig. 1). The lack of observation of any order down to the lowest explored temperature (50 mK $\sim J/3000$ —where J is the exchange interaction) [14–16] is a clear indication that this material is the best model quantum kagome antiferromagnet found to date.

Since the very first studies, there has been a debate about the actual low- T susceptibility χ , one of the most crucial tests of the low- T ground state. If the ground state is a singlet, χ should yield the singlet-triplet gap. However, the macroscopic susceptibility χ_{macro} , as measured by SQUID magnetometry, indicates a completely different situation,

with a monotonic increase down to $T = 0$ [15]. This response has been tentatively attributed to additional Dzyaloshinski-Moriya (DM) interactions [17]. An alternative explanation lies in the revelation of 5%–10% intersite exchange of Zn²⁺ and Cu²⁺, by powder neutron diffraction [18,19]; such an exchange could be responsible for a Schottky-like field dependent anomaly detected in the

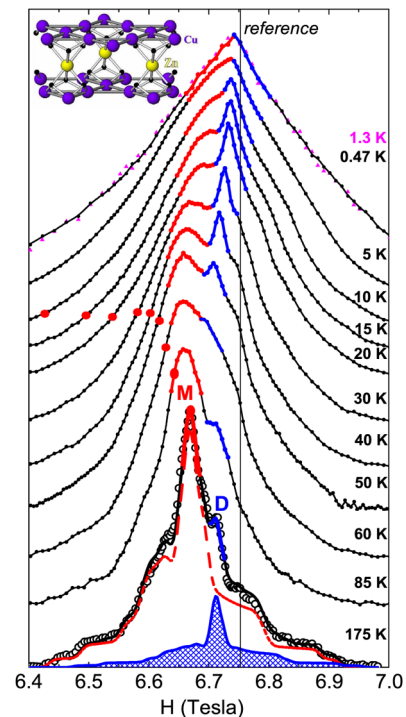


FIG. 1 (color online). ¹⁷O NMR spectra from 175 K to 0.47 K. The shift reference is indicated by the vertical line. The line on the 175 K spectrum is a simulation using two components, (M , dotted line) and (D , hatched); see text. Large full circles indicate the position of the center of the line that would be expected from χ_{macro} .

specific heat [19] and be the source of all or part of the low- T behavior of χ_{macro} [20]. This would result from both isolated Cu^{2+} spins on the Zn^{2+} site, which are weakly coupled to the kagome layers and nonmagnetic Zn^{2+} defects in the Cu^{2+} kagome planes, which are known to generate a specific spin texture in their vicinity as was suggested in former studies of magnetic dilution of frustrated lattices [21–23].

Local probe techniques, such as nuclear magnetic resonance (NMR), are invaluable to sort out the various contributions to χ . They enable one to map out a histogram of susceptibilities at various sites, otherwise summed up in χ_{macro} . ^{17}O NMR of enriched samples appears as the best compromise for such a local study. Because of the strong magnetic Cu-Cu coupling through the bridging oxygen, one can indeed safely expect that O couples predominantly to the 2 neighboring Cu sites of the kagome planes (Fig. 3) while its signal is not wiped out through relaxation effects, which is not the case for Cu [24]. For the first time, we are able to track accurately the susceptibility of the kagome lattice from 300 to 0.47 K; further, we clearly establish the existence of Zn/Cu substitution, and use the latter perturbation to reveal some novel aspects of the kagome physics around these defects. We also present a comparison of our ^{17}O NMR relaxation data with that from Cl and Cu sites [24], which suggests a nondispersive branch of low energy excitations.

The NMR experiments were performed on several unaligned powder samples of different origins, which gave identical results. Preparation and sample characterization follow standard routes described elsewhere [13,14] except that 50% ^{17}O enriched water was used for the preparation, and samples were not washed after filtration. ^{17}O NMR spectra were recorded from room- T down to 0.47 K by integrating the echo recorded by sweeping the field at a fixed frequency of 38.974 MHz. Delays between pulses were 10–20 μs , except in contrast experiments performed at low- T where delays, up to 200 μs , allow us to single out slowly relaxing sites. Quadrupolar and magnetic contributions were separated by taking additional spectra at 19.974 and 29.974 MHz. Quadrupolar singularities typical of a powder pattern are easily observed on the wings of our spectra at high- T (Fig. 1), and both a quadrupolar frequency $\nu_Q = 0.70(3)$ MHz and the asymmetry parameter $\eta = 0.64(10)$ were determined by the extreme cutoffs in the powder pattern ($^{17}\text{I} = 5/2$). The T_1 recovery curves were obtained by irradiating the main line with a train of 5 pulses separated by $\sim T_2$. Each component mixes all nuclear transitions (powder pattern), and we fixed the coefficients of the recovery law at the $T = 70$ K values.

In the present Letter, we track the evolution of the central part of the NMR spectrum. In the ideal case of a fully occupied Cu^{2+} kagome plane, the structure yields a single environment of the O site; therefore, one should observe a unique central $-1/2 \rightarrow 1/2$ sharp singularity in the high- T range, the shift of which reflects the suscep-

tibility of the two neighboring Cu^{2+} . However, two different lines rather than one, both corresponding to central transitions, are unexpectedly evident in our $T = 175$ K spectrum [(M) and (D) in Fig. 1; see also Fig. 2].

This clearly indicates the existence of *two* distinct local magnetic environments. The ratio of the magnetic shifts for the two lines (M) and (D) is ~ 2 , which naturally supports the association of the most shifted and most intense line with the vast majority of O nuclei locally coupled to two magnetic Cu^{2+} , while for the other line (D), O couples to only one Cu^{2+} , with the other neighboring site occupied by Zn. Since for each Zn at a Cu site of the kagome plane four O atoms are affected, the 20(5)% intensity of this line is found to be consistent with the 6(2)% Zn/Cu substitution suggested by other techniques [18–20].

The shift of both lines, $K^{(D)}$ and $K^{(M)}$, can easily be tracked over a broad T range. The main line (M) gives access to the intrinsic susceptibility of the kagome lattice through the line position, while the physics of a Cu first near neighbor of a nonmagnetic defect is best probed through the other line (D). The positions of the (M) and (D) lines were found to scale with the field after correction of second order quadrupolar effects for low frequencies, which proves their magnetic origin. No simulation could account for the presence of these two peaks in a single O site model even when different axes for the electric field gradient and shift tensors were allowed.

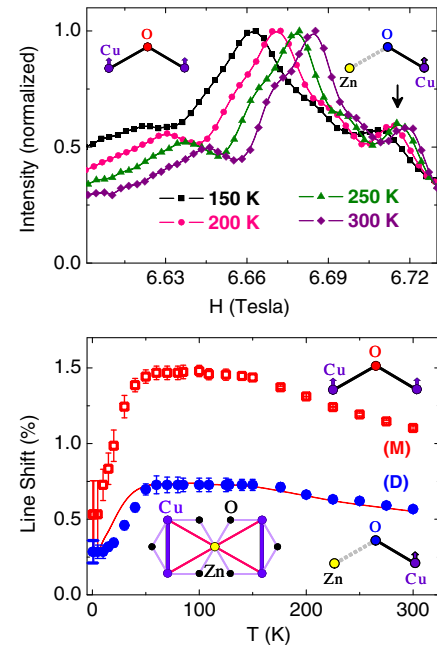


FIG. 2 (color online). Top: details of the high- T spectra. The shift of the main and defect lines are evident and found to be different. Bottom: Plot of the magnetic shift of both lines versus T . The line through the $K^{(D)}$ plot represents $K^{(M)}/2$. The sketch in the lower left corner illustrates the environment of a Zn substituted on the Cu kagome plane at $T = 0$, and thick lines represent Cu-Cu dimers.

The (M) line is found to shift towards low fields (increase of susceptibility) between 300 and 100 K [Fig. 2(a)], goes through a maximum between 100 and 50 K, and then progressively moves back towards the reference below 40 K while a rapid increase of the width occurs (Fig. 1). In the low- T regime, below 5 K, the linewidth tends to saturate and no difference was found between spectra taken at 1.3 and 0.47 K. The variation of the shift, $K^{(M)}$, is reported in Fig. 2(b). This relates to the T evolution of the susceptibility of Cu in the kagome planes, except those sitting close to nonmagnetic defects, through $K^{(M)} = 2A\chi_{\text{Cu}}$, where the hyperfine constant $A = 35(2)$ kOe/ μ_B [25]. It is worth noting that this coupling value is approximately 30 times larger than those reported for Cl NMR and μSR experiments, hence the invaluable sensitivity of the ^{17}O probe.

Two main model-free results can be deduced from $K^{(M)}$. (i) A maximum of the kagome susceptibility occurs around $J/2$, which differs markedly from χ_{macro} . Defects induced by Cu/Zn substitution and responsible for the low T increase of χ_{macro} contribute to the NMR linewidth. (ii) The susceptibility reaches a nonzero value at low T , typically $1/3$ of the maximum value, which indicates the absence of a spin gap in herbertsmithite.

One can invoke three possible scenarios. (i) A *nonsinglet* ground state of the ideal kagome system, such as appears to be the case here, with a decreasing susceptibility at low T associated with the strengthening of the AFM correlations below $T \approx J/2$, which then level off as $T \rightarrow 0$, and surprisingly, do not yield a gapped ground state. (ii) A *singlet-triplet gap*: The observation that the $T = 0$ susceptibility is finite in herbertsmithite could arise from a filling of the hypothetical gap—expected to be at most $J/20$ —under the modest applied field 6.5 T of our experiment. It is, however, not clear to us whether the magnetic energy brought to the system $\sim J/30$ should be compared to the gap value or to the larger one at which a magnetization plateau should occur. In addition, the value of the maximum of $K^{(M)}$ around 50 K is not in line with the expected small value of the gap. (iii) The existence of an additional DM interaction, $\vec{D} \cdot (\vec{S}_i \times \vec{S}_j)$, between Cu^{2+} spins that results from the absence of an inversion center between Cu ions, as suggested earlier [17]. This would modify the $T = 0$ susceptibility by *mixing singlet and triplet* states. Although χ could not be calculated below $0.25J$ [17], we anticipate from a comparison of our $K^{(M)}$ curve and [17] that this DM term might be smaller than suggested and rather less than $0.05J$, at least for one component of \vec{D} . Finally, one should point out that exact calculations, reliable down to $0.2\text{--}0.3J$, do not indicate any maximum in χ [26]. The deviation of our experimental data from the ideal case could be attributed either to the DM interaction or to the rather strong dilution of the network, favoring a dimerization of the ground state (see below).

We now turn to the defect line (D), which reflects the susceptibility of a Cu^{2+} in the immediate vicinity of a

nonmagnetic Zn^{2+} substituted on a kagome site. At high- T , the (D) line follows a trend similar to the (M) line, as can be observed through the comparison of spectra taken between 300 and 150 K [Fig. 2(a)]. The 1:2 scaling of $K^{(D)}$ with $K^{(M)}$ [Fig. 2(b)] indicates that in this T range defects have negligible effect on the Cu sites in their immediate vicinity, which underlines the shortness of the correlation length even for $T \sim J$, another well-known hallmark of frustration. The (D) line surprisingly appears below 50 K as a sharp prominent feature of the overall spectrum, which contrasts with the broadening of the (M) line in the same T range (Fig. 1). This relative narrowness points to a reduced distribution of susceptibilities, indicating a specific environment around the defect. In addition, below 50 K, the decrease of the shift is found to be sharper than for the (M) line, an indication that the susceptibility of Cu in the neighborhood of a Zn defect decreases faster. Finally, the transverse relaxation was found to be substantially longer than for the (M) line in this T range, which enabled us to perform contrast experiments and better isolate the defect line. A relative intensity of the (D) line $\sim 30(4)\%$ can then be calculated.

The picture that now emerges differs markedly from the situation met in nonfrustrated AFMs where the spin response is commonly enhanced in the immediate vicinity of a nonmagnetic defect [27] and would yield a rapid low- T increase of $K^{(D)}$ rather than the decrease clearly observed here. Our findings are in qualitative agreement with the results from exact diagonalizations where a defect is found to induce a significantly reduced susceptibility or even singlets on the 4 neighboring sites while an enhanced staggered susceptibility is induced for further neighbors [22]. The latter would be naturally responsible for the smoothing out of the quadrupolar singularities and could explain part or all of the broadening of the (M) line. Another source of broadening could also result from the alternating DM contribution as proposed recently [17]. In the ideal case of singlets induced around a nonmagnetic defect, a simple counting argument yields 6 O sites per defect (Fig. 2(b)) with a zero shift, therefore 36% of the O sites are affected, in agreement with the detected intensity. The sharper decrease of $K^{(D)}$ compared to $K^{(M)}$, could therefore be explained by a tendency for Cu to dimerize near a defect, as expected from the local relief of frustration. The fact that we do not observe a zero-susceptibility and a gap resulting from dimers could certainly be ascribed again to DM interactions.

Finally, T_1 measurements performed at the (M) peak yield information about the excitations. A second smaller contribution, likely due to the proximity of the (D) line, was found below 50 K, with a T_1 , which gets longer when T is lowered. This certainly corroborates the decrease of magnetic effects in the vicinity of a Zn defect, as already suggested by our shift data. In Fig. 3, we plot the main contribution below 70 K, dominated by the physics of the kagome plane, and compare it to existing Cl and O NMR

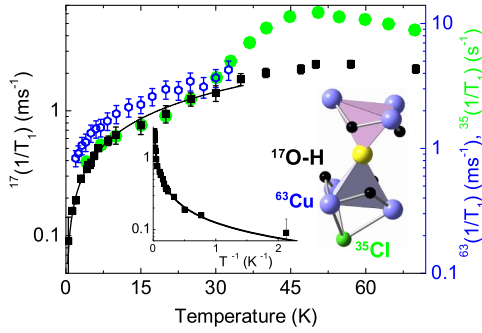


FIG. 3 (color online). Semilogarithmic T_1^{-1} plots for ^{17}O (this work) and for ^{63}Cu and ^{35}Cl [24]. The similarity of the T variation for the 3 nuclei is evident. Inset: ^{17}O T_1^{-1} versus T^{-1} . A nonzero gap would yield a linear variation, not observed here.

data [24]. Between 70 and 30 K, we do not find a marked maximum such as observed for Cl NMR, which had been suggested to be of structural origin. Because of its weak quadrupolar moment and its larger coupling constant to Cu, ^{17}O NMR is less sensitive to structural effects and mainly probes magnetic properties. Whatever the origin of the $^{35}(1/T_1)$ peak, our data indicate that magnetic properties are not affected. As for Cu T_1^{-1} , we find a downward curvature of our data below 20 K and the inset of Fig. 3 clearly shows that the excitations are *not gapped*. The absence of an anomaly in the T_1 variation is in line with the absence of a signature of a transition as observed in our shift measurements down to 0.47 K or in earlier measurements [14–16]. We rather find that $T_1^{-1} \sim T^{0.73(5)}$ and the perfect agreement of all data taken on various probes with different local q -space filtering of fluctuations is a clear experimental indication that the excitation modes responsible for this relaxation are dispersionless as suggested for a long time [28]. One would indeed expect that “triangular 120° ” modes or (π, π) modes are filtered out and do not contribute to the relaxation, respectively, at the Cl or O sites in contrast to what happens at the Cu sites.

To summarize, we demonstrate the existence of a maximum in the susceptibility at $\sim J/2$, which is certainly related to the kagome physics and also observed in other corner-sharing kagome based lattices [21,23,29]. A rapid decrease of the susceptibility to a finite value at low- T and ungapped excitations point at a nonsinglet ground state in herbertsmithite. The excitations do not have a marked structure in q -space, a hallmark of frustration. A depressed susceptibility is observed for Cu next to defects. This response is certainly specific to the kagome physics and observed here for the first time. It opens the route for revealing intrinsic physics through magnetic perturbations after a better control of Zn/Cu substitution is achieved. In order to clarify whether a gap would occur in ideal kagome Heisenberg AFM, an accurate experimental determination

of the DM term is necessary and the search for a zero-defect “second generation” compound guides future experimental work.

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